

## Enantiofacial Discrimination in Dihapto-Coordination of Aromatic Molecules by the Chiral $\pi$ -Base/ $\sigma$ -Lewis Acid {TpRe(CO)(PMe<sub>3</sub>)}

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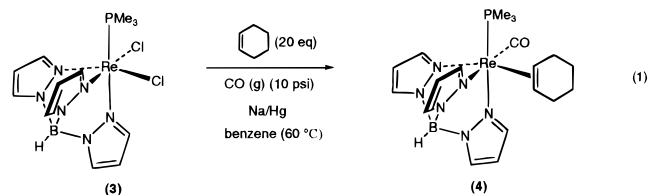
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Aromatic compounds constitute a diverse and abundant source of cyclic carbon skeletons that may be incorporated into the synthesis of many natural products and biologically important molecules. However, the inherent stability of these compounds often limits the scope of their useful chemical transformations. One strategy used to overcome this aromatic “inertia” has been to complex these molecules with a transition metal. Exhibiting chemistry that is complementary to that of  $\eta^6$ -aromatic complexes,<sup>1</sup> the pentaammineosmium(II) fragment binds aromatic compounds in a dihapto-coordination mode and activates the ligand toward electrophilic addition.<sup>2</sup> Although the  $\{(NH_3)_5Os\}^{2+}$  system has been utilized for a wide variety of arene substitution and dearomatization transformations, this chemistry has been limited to racemic mixtures due to the inaccessibility of chiral derivatives of the pentaammineosmium(II) system.<sup>3</sup> Our search for other metals which exhibit binding and activation features similar to osmium,<sup>4,5</sup> yet would tolerate a more diverse set of ligands, prompted the exploration of the {TpRe(CO)<sub>2</sub>} (Tp = hydridotris(pyrazolyl)borate) fragment.<sup>6,7</sup> Although we were unsuccessful in obtaining mononuclear complexes suitable for dearomatization reactions, complexes of the type  $\{[TpRe(CO)_2]_2-(\mu-\eta^2:\eta^2-A)\}$  (where A = furan, *N*-methylpyrrole, naphthalene, or dinitrobenzene) were isolated and characterized. We reasoned that, since these binuclear species were likely formed via aromatic ligand dissociation from the transient monomeric complexes TpRe(CO)<sub>2</sub>( $\eta^2$ -A), more stable aromatic complexes could be obtained by substituting one of the CO ligands of {TpRe(CO)<sub>2</sub>} with a weaker  $\pi$ -acid or stronger  $\sigma$ -donor.

Mayer and Brown have demonstrated that TpRe(Cl)<sub>2</sub>(pyridine) can be synthesized from TpRe<sup>V</sup>(Cl)<sub>2</sub>(O) (**1**).<sup>8</sup> The synthetic sequence involves the initial reduction of the Re(V) oxo complex **1** to Re(III) with triphenylphosphine. Similarly, the addition of trimethylphosphine to **1** yields the bright orange phosphineoxide complex TpRe<sup>III</sup>(Cl)<sub>2</sub>(O=PMe<sub>3</sub>) (**2**) (93%). In refluxing DME

(DME = 1,2-dimethoxyethane), the phosphineoxide ligand of **2** is labile, and reaction with excess L (where L = PMe<sub>3</sub>, NH<sub>3</sub>, P(OMe)<sub>3</sub>, <sup>t</sup>BuNC, pyridine, etc.) yields the corresponding TpRe<sup>III</sup>-(Cl)<sub>2</sub>(L) complexes in good yield. To increase the chances of obtaining high enantiofacial differentiation upon  $\eta^2$  binding of prochiral aromatic compounds, we sought a complex containing a single, bulky ligand which could be elaborated into the corresponding monocarbonyl complex. Therefore, TpRe(Cl)<sub>2</sub>(PMe<sub>3</sub>) (**3**), which is prepared as an orange solid in 85% yield from **2** and PMe<sub>3</sub>, was selected. The reduction of **3** from Re<sup>III</sup> to Re<sup>I</sup> (Na/Hg) in a pressure tube under CO(g) (10 psi) in the presence of 20 equiv of cyclohexene (benzene solvent, 60 °C) yields TpRe<sup>I</sup>(CO)(PMe<sub>3</sub>)( $\eta^2$ -cyclohexene) (**4**) (56%) (eq 1). The



production of a small amount of TpRe(CO)<sub>2</sub>(PMe<sub>3</sub>) and TpRe-(CO)<sub>2</sub>( $\eta^2$ -cyclohexene) (approximately 10% total) slightly reduces the yield of **4**. Notable features of complex **4** include a low-energy CO stretching absorption at 1796 cm<sup>-1</sup> (KBr) in the infrared spectrum, a chemically and electrochemically reversible oxidation (Re<sup>II</sup>/Re<sup>I</sup>) at 0.23 V (vs NHE; 100 mV/s) in the cyclic voltammogram, resonances at 51.0 and 48.6 ppm (<sup>13</sup>C NMR) assigned to the bound olefinic carbons, and a singlet in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum at -18.09 ppm.<sup>9</sup>

To maximize the overlap between the olefin  $\pi^*$  orbital with the  $d\pi$  HOMO of the d<sup>6</sup> rhenium center, the geometry of the olefinic bond was expected to be orthogonal to the Re–CO bond axis.<sup>10</sup> The solid-state structural determination of **4** (ORTEP drawing in Supporting Information) confirms this geometry where the olefinic bond is found to be nearly parallel to the Re–P bond axis.<sup>11,12</sup>

Treatment of **4** with AgOTf (OTf = trifluoromethanesulfonate) yields a green solution which displays a single CO absorption at 1912 cm<sup>-1</sup>. This new complex is presumed to be the one-electron oxidation product [TpRe(CO)(PMe<sub>3</sub>)( $\eta^2$ -cyclohexene)][OTf] (**5**). After 30 min of refluxing in DME, the absorption at 1912 cm<sup>-1</sup> is replaced by a new peak at 1866 cm<sup>-1</sup>. The IR features of this reaction likely correspond to cyclohexene dissociation and the formation of TpRe(CO)(PMe<sub>3</sub>)(OTf) (**6**).

The reduction of **6** in the presence of excess naphthalene, thiophene, or furan yields stable mononuclear complexes of the form TpRe(CO)(PMe<sub>3</sub>)( $\eta^2$ -L) {L = naphthalene (**7**) (55%), thiophene (**8**) (77%), or furan (**9**) (81%)} (Scheme 1). The direct substitution of an aromatic compound for cyclohexene at the Re-(I) oxidation state is difficult due to the thermal stability of **4** as well as the instability of **7–9** at high temperatures. Of particular significance is the  $\eta^2$  bound naphthalene complex of which examples are extremely rare.<sup>4</sup> <sup>1</sup>H and <sup>13</sup>C NMR data indicate that the metal binds exclusively across C1 and C2. Monitoring a  $d_{\sigma}$ -

(9) The phosphorous chemical shifts of the Re(I) complexes reported herein are similar to previously reported Re(I)–PMe<sub>3</sub> complexes. For example, see: Cusanelli, A.; Sutton, D. *Organometallics* **1995**, *14*, 4651.

(10) Back-bonding of the two  $d\pi$  orbitals which are oriented along the Re–CO bond axis with the strongly  $\pi$ -acidic CO ligands will result in substantial lowering of the energy of these two orbitals.

(11) For reports of structural features of similar rhenium–alkene complexes, see: (a) Kowalczyk, J. J.; Arif, A. M.; Gladysz, J. A. *Chem. Ber.* **1991**, *124*, 729. (b) Pu, J.; Peng, T.-S.; Mayne, C. L.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 2686.

(12) The majority of the protons of complex **4** were located in the Fourier map. However, due possibly to disorder, H(3) and H(17) were not located in the Fourier map, and these hydrogens were placed at calculated positions.

(1) See, for example: (a) Semmelhack, M. F. *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 8, p 489. (b) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Mill Valley, CA, 1994, Chapter 10.

(2) Harman, W. D. *Chem. Rev.* **1997**, *97*, 1953.

(3) The inability to manipulate the ligand set without disrupting the binding affinity of this fragment precludes the use of a chiral metal to direct stereoselective reactions with Os<sup>II</sup>. For attempts to alter the ligand set of  $\{(NH_3)_5Os\}^{2+}$ , see: (a) Barrera, J.; Orth, S. D.; Harman, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 7316. (b) Orth, S. D.; Barrera, J.; Rowe, S. M.; Helberg, L. E.; Harman, W. D. *Inorg. Chim. Acta* **1998**, *270*, 337. In addition, the dicationic nature limits solvent environments and purification techniques.

(4) Reports of stable  $\eta^2$ -aromatic complexes are rare. For examples of dihapto-bound aromatic complexes, see ref 6.

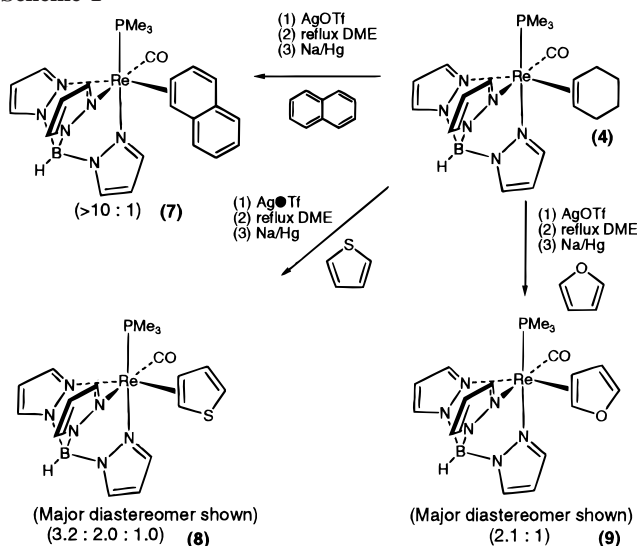
(5) Helberg, L. E.; Orth, S. D.; Sabat, M.; Harman, W. D. *Inorg. Chem.* **1996**, *35*, 5584; Brooks, B. C.; Chin, R. M.; Harman, W. D. *Organometallics* **1998**, *17*, 4716.

(6) Gunnoe, T. B.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 8747.

(7) For recent reviews of hydridotris(pyrazolyl)borate ligands, see: (a) Kitajima, N.; Tolman, W. D. *Prog. Inorg. Chem.* **1995**, *43*, 419. (b) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943. (c) Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 115.

(8) (a) TpRe(Cl)<sub>2</sub>(O) was first reported in Abrams, M. J.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1984**, *82*, 125. (b) Mayer and Brown have reported an improved synthesis: Brown, S. N.; Mayer, J. M. *Inorg. Chem.* **1992**, *31*, 4091. (c) This reaction sequence is similar to a synthesis of TpRe-(Cl)<sub>2</sub>(pyridine) reported by Mayer and Brown: Brown, S. N.; Mayer, J. M. *Organometallics* **1995**, *14*, 2951.

## Scheme 1

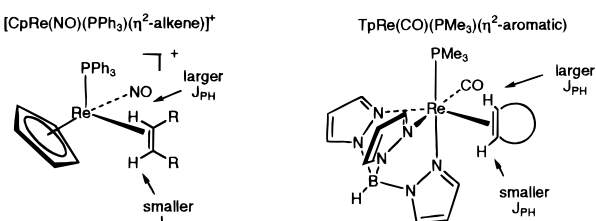


acetone solution of **7** by  $^1\text{H}$  NMR indicates that the naphthalene complex undergoes a clean substitution reaction with the solvent ( $t_{1/2} \approx 8$  h). Nearly quantitative appearance of free naphthalene is accompanied by the formation of a single new TpRe complex  $\{\text{TpRe}(\text{CO})(\text{PMe}_3)(\eta^2\text{-acetone})$  (**10**). Independent synthesis of the acetone complex **10** confirms the identity of the exchange product (see Supporting Information for details). Of note, it is difficult to access complexes **7–9** by direct reduction of  $\text{TpRe}(\text{Cl})_2(\text{PMe}_3)$  (**3**) under CO (g) in the presence of the corresponding aromatic due to the thermal conditions required for halide loss (i.e., the dihapto-bound aromatic products are not stable under the reaction conditions).

Only one diastereomer is detected by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR data for the naphthalene complex **7**. Diastereomer interconversion is expected to be rapid for **7** like that of its osmium analogue,<sup>13</sup> thus the observation of only a single diastereomer should reflect a thermodynamic bias for the binding of a single enantioface. Stereoisomer exchange rapid enough to result in a time-averaged  $^1\text{H}$  NMR spectrum of two diastereomers seems highly unlikely given the observation of well-resolved diastereomers for analogous rhenium systems.<sup>13</sup> As is the case for the olefinic ligand in **4**, the naphthalene C1–C2 bond is expected to be aligned approximately parallel with the Re–P bond axis. Whereas the pyrazolyl ring trans to the CO effectively directs the ligand away from it (and syn to the CO ligand), the steric influence of the phosphine appears to dominate that of the pyrazolyl ring trans to it. Thus, NOE and P–H coupling data (vide infra) indicate that the B ring of the naphthalene ligand (i.e., the uncomplexed ring) is oriented away from the phosphine ligand.

The rhenium fragment  $\{\text{Cp}^x\text{Re}(\text{NO})(\text{PPh}_3)\}^+$  ( $\text{Cp}^x =$  cyclopentadienyl or pentamethylcyclopentadienyl) is closely related to the  $\{\text{TpRe}(\text{CO})(\text{PMe}_3)\}$  system, and Gladysz et al. have extensively studied the enantiofacial binding preferences of the  $\text{Cp}^x$  systems.<sup>14</sup> Significantly, large differences in phosphine–hydrogen coupling constants for  $[\text{Cp}^x\text{Re}(\text{NO})(\text{PPh}_3)(\eta^2\text{-alkene})]^+$  complexes are observed for the protons of the bound carbons. In particular, the olefinic proton(s) oriented toward the phosphine display  $J_{\text{PH}}$  values that are dramatically larger than those oriented away from the phosphine (Scheme 2).<sup>14b</sup> An analogous difference in coupling constants is observed for compounds **7**, **8**, and **9** (Scheme 2). Accordingly, by using the combination of coupling constants, NOE data, and  $^1\text{H}$  decoupling experiments unambiguous assignment of major and minor coordination diastereomers for these com-

## Scheme 2



plexes was possible, and the former are shown in Scheme 1.<sup>15</sup>

Regarding the significance of the heterocyclic complexes **8** and **9**, reports of  $\eta^2$ -thiophene and  $\eta^2$ -furan complexes are scarce. Although thiophene exhibits a diversity of coordination modes,<sup>16</sup> examples of dihapto-coordinated thiophenes are rare. It has been suggested that sulfur-bound thiophene–metal bonds are dominated by the heteroatom-to-metal  $\sigma$ -bonding contribution, and that  $\eta^1$ -thiophene is a relatively poor  $\pi$ -acid.<sup>17</sup> Spectroscopic evidence ( $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR) indicates that **8** exists as a 3.2/2.0/1.0 mixture of isomers (22 °C). These isomers have been assigned as two  $\eta^2$ -bound diastereomers and the  $\eta^1$ -sulfur bound complex ( $\eta^2/\eta^1 = 5.2/1.0$ ). The thermodynamic stability of the  $\eta^2$  coordination mode compared to the  $\eta^1$  coordination mode is a reflection of the  $\pi$ -basicity of the  $\{\text{TpRe}(\text{CO})(\text{PMe}_3)\}$  fragment. Similar to the thiophene complex **8**, the furan complex **9** exists as a mixture of isomers (2.1/1.0 ratio; 22 °C). However, for furan the  $\eta^1$ -heteroatom bound coordination mode is absent. For  $\pi$  bound isomers **8** and **9** there is a slight preference to have the heteroatom oriented away from the phosphine, but the stereo-differentiation is much lower than that for naphthalene. The differences between the two enantiofaces of these prochiral heterocycles are small, and the modest diastereoselectivity is likely a reflection of this negligible steric difference rather than of poor chiral discriminating ability of the metal system.

Although details of the elaboration of the naphthalene ligand are beyond the scope of the current study, preliminary data indicate that, when subjected to an acidic solution of a 1-methoxy-2-methyl-1-trimethylsilyloxypropene, it undergoes 1,4-addition to give a single diastereomer of a 1,4-dihydronaphthalene complex analogous to that observed for osmium.<sup>18</sup> Oxidation of this complex with AgOTf results in the observation of the free 1,4-dihydronaphthalene compound.

In summary, a synthetic route to the  $\pi$ -basic  $\{\text{TpRe}(\text{CO})(\text{PMe}_3)\}$  fragment has been developed. This metal system forms stable  $\eta^2$ -aromatic complexes with naphthalene, thiophene, and furan that approach the stability of the pentaammineosmium(II) system. While the chiral metal fragment demonstrates only modest ability to discriminate enantiofaces with the heterocycles thiophene and furan, excellent stereo-differentiation is achieved upon coordination of naphthalene. Thus, it is possible that an entirely new class of dearomatization agents may be obtained of the form  $\{\text{TpRe}(\text{CO})(\text{L})\}$  that may ultimately prove to be powerful tools for the synthetic chemist.

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**Supporting Information Available:** Synthetic procedures and full characterization data for complexes **1–4** and **7–9**, details of the X-ray diffraction study, a labeled ORTEP diagram, crystal and refinement data, bond lengths and angles, atomic coordinates and anisotropic displacement parameters (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA990891E

(15) For full details of these studies, see the Supporting Information.

(16) (a) Angelici, R. J. *Coord. Chem. Rev.* **1990**, *105*, 61. (b) Choi, M.-G.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 7811 and references therein.

(17) (a) Harris, S. *Organometallics* **1994**, *13*, 2628. (b) Palmer, M. S.; Rowe, S.; Harris, S. *Organometallics* **1998**, *17*, 3798.

(18) (a) Winemiller, M. D.; Harman, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 7835. (b) See Supporting Information for details.

(13)  $[\text{ReTp}(\text{CO})(\text{L})(\text{naphthalene})]$  complexes (where L = pyridine and *tert*-butylisonitrile) have also been prepared recently in our laboratories. These systems show two resolved diastereomers at 20 °C.

(14) (a) Gladysz, J. A.; Boone, B. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 550. (b) See p 557 of ref 14(a).